Rejuvenation of 248 nm Resist Backbones for 157 nm Lithography

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Fluorocarinol-based acrylic and styrenic monomers, such as 2-[4-(2-hydroxyhexafluoroisopropyl)cyclohexane]hexafluoroisopropyl acrylate (1) 2-[4-(2,2,2-trifluoro-1-methoxymethoxy-1-trifluoromethylethyl)cyclohexane]hexafluoroisopropyl acrylate (2), and 2-[4-(2,2,2-trifluoro-1-ethoxymethoxy-1-trifluoromethylethyl)]styrene (3), were synthesized and their (co)polymers were studied as photoresist platforms for 157 nm lithography. It was found that these (co)polymers are unusually transparent at 157 nm, and absorbances of poly(1) and poly(1-co-3) were determined to be 1.93 and 2.38 μm^{-1} , respectively. It was also found that further improvement in transparency is possible by adding *transparency enhancers* to the resist platform. Lithographic studies were carried out with poly(1)- and poly(3)-based resists using 157 and 248 nm steppers, and it was proven that, after selective modification, it is possible to use conventional resist backbones, such as acrylic or styrenic, in the design of single-layer resists for 157 nm lithography.

Keywords: 157 nm resists, fluorocarinol, transparency enhancers

1. Introduction

One of the most challenging issues in the design of photoresists for 157 nm lithography has been the transparency of the polymer platforms. [1] Although protected phenols and carboxylic acids are indispensable structural units in the design of chemically amplified resists for 248 and 193 nm applications, these acidic functions absorb too strongly at 157 nm. Therefore, fluorocarinol functionalized polymers have garnered much interest due to their transparency at 157 nm combined with their comparable acidity to phenols. [2,3]

In order to develop single-layer resists for 157 nm lithography, we exploited a variety of fluorocarinol containing polymers [4-6] as well as conventional resist platforms such as styrenic and acrylic polymers. We found that the transparency of conventional resist platforms can be greatly enhanced at 157 nm by judicious modification of highly absorbing groups such as aromatic or

carbonyl functions. In this paper, we report our strategy to develop highly transparent resist platforms for single-layer resist applications at 157 nm lithography.

2. Experimental

2.1. Instrumentation

¹H NMR and ¹³C NMR spectra were recorded on Varian Inova-400 and Varian VXR-400s spectrometers, respectively. Thermogravimetric analysis (TGA) was performed on a Seiko TG/DTA 220 system at a heating rate of 10 °C/min. Optical spectra of the polymer films were recorded on a VU-301 vacuum ultraviolet variable angle spectroscopic ellipsometer (VUV-VASE) instrument (J. A. Woollam Co.) at International SEMATECH. Samples for VUV-VASE measurements were prepared by spin-coating resists on a silicon wafer, primed with hexamethyldisilazane (HMDS) gas, followed by soft-bake at 115 °C for 120 sec.

2.2. Synthesis of 2-[4-(2-hydroxyhexafluoroisopropyl)cyclohexane]hexafluoroisopropyl acrylate (1)

To a solution of 1,4-bis(2-hydroxyhexafluoroisopropyl)cyclohexane (30.0 g, 0.07 mol) in 100 mL of dry THF, was added 45 mL of 1.6 M *n*-butyllithium (0.07 mol) under nitrogen over a period of 30 min. After 2 h, the resulting solution was treated during 30 min by the dropwise addition of acryloyl chloride (6.5 g, 0.07 mol) dissolved in 100 mL of dry THF. The resulting solution was stirred overnight at room temperature and hydrolyzed by the addition of 100 mL of distilled water. The aqueous phase was extracted with ethyl ether, and the combined organic phase was dried over MgSO_4 . The crude product was purified by column chromatography and recrystallization to yield 15.9 g (49% yield): mp 85–86.4 °C; ^1H NMR(CDCl_3 , 400 MHz) δ 6.48 (dd, 1H, $\text{CHH}_{\text{cis}}=\text{CH}-$), 6.12 (q, 1H, $\text{CH}_2=\text{CH}-$), 5.98 (dd, 1H, $\text{CHH}_{\text{trans}}=\text{CH}-$), 3.20–3.15 (m, methine H, adjacent to ester), 3.05 (s, 1H, -OH), 2.27–2.21 (m, 1H, methine H, adjacent to hydroxyl), 2.05–1.98 (m, 2H, methylene H in the ring), 1.93–1.83 (m, 2H, methylene H in the ring), 1.70–1.59 (m, 4H, methylene H in the ring); ^{13}C NMR(CDCl_3 , 100 MHz) δ 162.11 (C=O), 133.97 ($\text{CH}_2=\text{CH}-$), 126.95 ($\text{CH}_2=\text{CH}-$), 123.44 (quartet, $-\text{C}(=\text{O})\text{OC}(\text{CF}_3)_2-$, $J_{\text{C-F}} = 288$ Hz), 122.24 (quartet, $-\text{C}(\text{CF}_3)_2\text{OH}$, $J_{\text{C-F}} = 288$ Hz), 85.33 (septet, $-\text{C}(=\text{O})\text{OC}(\text{CF}_3)_2-$, $J_{\text{C-C-F}} = 29$ Hz), 79.01 (septet, $-\text{C}(\text{CF}_3)_2\text{OH}$, $J_{\text{C-C-F}} = 27$ Hz), 34.64 (methine C adjacent to ester), 34.00 (methine C adjacent to hydroxyl), 24.01 (methylene C adjacent to ester), 21.89 (methylene C adjacent to hydroxyl); ^{19}F NMR (CDCl_3 , 376 MHz, CFCl_3): δ -68.35 ($-\text{C}(=\text{O})\text{OC}(\text{CF}_3)_2-$), -74.30 ($-\text{C}(\text{CF}_3)_2\text{OH}$).

2.3. Synthesis of 2-[4-(2,2,2-trifluoro-1-methoxy-methoxy-1-trifluoromethylethyl)cyclohexane]hexafluoroisopropyl acrylate (2)

To a dispersion of sodium hydride (0.28 g) in dry THF (15 mL), was added 4.7 g of 1 (0.01 mol) dissolved in dry THF (15 mL) at 0 °C. After stirring for 1 h at room temperature, chloromethyl methyl ether (0.89 g, 0.011 mol) in 20 mL of dry THF was added dropwise over a period of 30 min at 0 °C. The resulting solution was stirred overnight at room temperature and hydrolyzed by the addition of distilled water. The aqueous phase was extracted with ethyl ether, and the combined organic phase was dried over MgSO_4 . The crude product was purified by column chromatography to yield 2.4 g of pure 2 (51% yield): ^1H NMR (CDCl_3 , 400 MHz) δ 6.48 (dd, 1H, $\text{CHH}_{\text{cis}}=\text{CH}-$),

6.12 (q, 1H, $\text{CH}_2=\text{CH}-$), 5.98 (dd, 1H, $\text{CHH}_{\text{trans}}=\text{CH}-$), 4.93 (s, 2H, $-\text{OCH}_2\text{O}-$), 3.44 (s, 3H, $-\text{OCH}_3$), 3.23–3.17 (m, methine H, adjacent to ester), 2.34–2.29 (m, 1H, methine H, adjacent to ether), 2.05–1.99 (m, 2H, methylene H in the ring), 1.92–1.86 (m, 2H, methylene H in the ring), 1.67–1.56 (m, 4H, methylene H in the ring); ^{13}C NMR(CDCl_3 , 100 MHz) δ 161.89 (C=O), 133.87 ($\text{CH}_2=\text{CH}-$), 127.01 ($\text{CH}_2=\text{CH}-$), 123.27 (quartet, $-\text{C}(=\text{O})\text{OC}(\text{CF}_3)_2-$, $J_{\text{C-F}} = 290$ Hz), 122.29 (quartet, $-\text{C}(\text{CF}_3)_2\text{OCH}_2-$, $J_{\text{C-F}} = 293$ Hz), 93.95 ($-\text{OCH}_2\text{O}-$), 85.27 (septet, $-\text{C}(=\text{O})\text{OC}(\text{CF}_3)_2-$, $J_{\text{C-C-F}} = 28$ Hz), 82.84 (septet, $-\text{C}(\text{CF}_3)_2\text{OCH}_2\text{O}$, $J_{\text{C-C-F}} = 27$ Hz), 57.13 ($-\text{OCH}_3$), 34.48 (methine C adjacent to ester), 34.29 (methine C adjacent to ether), 24.02 (methylene C adjacent to ester), 21.66 (methylene C adjacent to ether); ^{19}F NMR (CDCl_3 , 376 MHz, CFCl_3): δ -68.51.

2.4. Synthesis 2-[4-(2,2,2-trifluoro-1-ethoxy-methoxy-1-trifluoromethylethyl)]styrene (3)

4-(2-Hydroxy hexafluoroisopropyl)styrene was synthesized using a modified procedure reported by Snow et al.[7] The protection reaction of a hydroxyl group was carried out using chloromethyl methyl ether as described for 2: ^1H NMR(CDCl_3 , 400 MHz) δ 7.52 (q, 4H, aromatic), 6.72 (q, 1H, $\text{CH}_2=\text{CH}-$), 5.82 (d, 1H, $\text{CHH}_{\text{cis}}=\text{CH}-$), 5.35 (d, 1H, $\text{CHH}_{\text{trans}}=\text{CH}-$), 4.87 (s, 2H, $-\text{OCH}_2\text{O}-$), 3.79 (q, 2H, $-\text{OCH}_2\text{CH}_3$, $J = 7$ Hz), 1.25 (t, 3H, $-\text{OCH}_2\text{CH}_3$, $J = 7$ Hz).

2.5. Polymerization

Radical (co)polymerization of fluorocarbonol monomers was carried out using 2,2'-azobisisobutyronitrile (AIBN) in THF. The calculated amounts of monomers, solvent, and initiator were charged into the polymerization tubes, which were then immersed in a Dewar flask containing liquid nitrogen. After three cycles of freeze-thaw treatment under N_2 , the tubes were sealed and placed in an oil bath at 70 °C for 24 h. Polymers were recovered by precipitation into distilled water and dried in vacuum at 50 °C.

2.6. Lithographic evaluation

Imaging experiments at 248 nm were carried out using a Nikon 248 nm stepper ($NA = 0.42$) equipped with a KrF excimer laser source. Copolymers were dissolved in propylene glycol methyl ether acetate (PGMEA) (~15 wt%) and to this was added triphenylsulfonium perfluoro-1-butanefluorobutanesulfonate (TPSNf) as PAG in 1–5 wt% with respect to the polymer weight. The solution was

Scheme 1

Figure 1. VUV-VASE spectrum of poly(1).

filtered through a 0.2 μm membrane filter and spin-coated onto silicon wafers either primed with HMDS gas or treated with antireflective coatings. Post-apply bake (PAB) was carried out at 115 $^{\circ}\text{C}$ for 90 sec. Post-exposure bake (PEB) was carried out at 90–130 $^{\circ}\text{C}$ for 60–90 sec, and development was conducted for 60 sec in 0.262 N tetramethylammonium hydroxide (TMAH) solution. The film thickness was measured on a Tenkor P-10 Surface Profiler and developed patterns were imaged with a Leo 982 (Zeiss) scanning electron microscope. Imaging experiments at 157 nm were carried out at International SEMATECH.

3. Results and Discussion

3.1. Acrylic Resist Platforms Highly Transparent at 157 nm

The synthesis of fluorocarbonol-functionalized acrylic monomers was carried out as shown in Scheme 1. This scheme allows the straightforward synthesis of various fluorocarbonol-containing acrylic monomers where R is H, F, Cl, or CF_3 . In order to examine the effect of fluoroalkyl groups on the absorbance of the acrylic backbone, monomer 1 (R = H) was polymerized by simple radical polymerization. The absorbance of the resulting poly(1) was measured using VUV-VASE. As shown in Figure 1, poly(1) exhibited extremely high transparency at 157 nm and the absorbance at this wavelength was found to be $1.93 \mu\text{m}^{-1}$. The

Figure 2. Absorbance of PMMA at 157 nm with various mole fraction of 1,4-bis(2-hydroxyhexafluoroisopropyl)cyclohexane with respect to the PMMA repeating unit.

unusually low absorbance of poly(1) can be accounted for in terms of the electronic structure of the carboxyl group as well as the volume effect of the trifluoromethyl group.

The effect on the electronic structure of the carboxyl group of geminal trifluoromethyl groups, incorporated on the β -position to the acrylate ester oxygen, can be readily seen from ^{13}C NMR spectroscopy. While the chemical shifts of carboxyl carbons in poly[alkyl (meth)acrylate)s are observed at ~ 175 ppm, the carboxyl carbon in poly(1) exhibits an upfield shift by ~ 5 ppm and the chemical shift is observed at ~ 170 ppm. This indicates that geminal CF_3 groups in the β -position to the acrylate ester oxygen induce significant changes in the electronic structure of the carboxyl carbon in poly(1), rendering the carbonyl chromophore less absorbing than expected at 157 nm.

Van der Waals volume of the CF_3 group was reported to be $42.6 \text{ \AA}^3$ and this is considerably larger than that of the CH_3 group which is $16.8 \text{ \AA}^3$. [8] Therefore, one can imagine that, with poly(1), the concentration of the ester group per unit volume is significantly diluted in the presence of four bulky CF_3 groups. In order to see the volume effect of the CF_3 group on the absorbance of acrylic backbones, 1,4-bis(2-hydroxyhexafluoroisopropyl)cyclohexane was mixed with poly(methyl methacrylate) (PMMA) and the absorbance was measured using VUV-VASE. Figure 2 shows the absorbance of PMMA at 157 nm with various mole fractions of 1,4-bis(2-hydroxyhexafluoroisopropyl)cyclohexane with respect to the PMMA repeating unit. When 50 mol% of 1,4-bis(2-hydroxyhexafluoroisopropyl)cyclohexane is mixed with

Figure 3. Expanded ^{13}C NMR (100 MHz, acetone- d_6) spectrum of poly(1-co-2).

PMMA, we can construct an imaginary polymer structure that has a chemical formula of poly(1) with extra $\text{C}_2\text{H}_8\text{O}$ elements per repeating units. From the linear fit of the data in Figure 2, it is calculated that this imaginary polymer has an absorbance of $3.11\ \mu\text{m}^{-1}$ at 157 nm, and a further decrease in absorbance can be expected by removing the extra $\text{C}_2\text{H}_8\text{O}$ elements per repeating units. This estimation indicates that the volume effect of the bulky CF_3 group cannot be ruled out in the explanation of the high transparency of poly(1). It is also notable that fluorocarbon-containing small molecules, such as 1,4-bis(2-hydroxyhexafluoroisopropyl)cyclohexane, can be used as *transparency enhancers* to reduce the absorbance of conventional resist platforms at 157 nm.

3.2. Synthesis of Fluorocarbon-Containing Acrylic Copolymers

The synthesis of chemically amplified resists for 157 nm lithography was carried out by the copolymerization of monomer 1 with monomer 2 ($\text{R} = \text{H}$) which has an acid labile protecting group. Although it remains to be proven, the following scheme is proposed for the chemical amplification of the methoxy methyl protecting group in the presence of a photo-acid generator (PAG).

methoxy methyl cation has been reported to possess large gaseous stabilization energy and its stabilization energy is 68 kcal, which is very close to 74 kcal for a *tert*-butyl cation.[9] It appears that

Figure 4. TGA traces of poly(1-co-2) (A) and after exposure to 248 nm in the presence of PAG (B).

the only pathway for chemical amplification is through the hydrolysis of the cation by adventitious moisture.

Figure 3 shows the expanded ^{13}C NMR spectrum of poly(1-co-2) with structural assignments. The chemical shifts of carboxyl carbon corresponding to racemic triads (*rr*) are observed at 169.98 ppm, and meso triads (*mr*) are observed at 168.41 ppm. This result indicates that radical copolymerization of 1 and 2 yields syndiotactic-rich poly(1-co-2).

Thermal stability of poly(1-co-2) was studied using TGA. The TGA traces of poly(1-co-2), with 28 mol% of monomer 2, are shown in Figure 4A, while Figure 4B shows the traces of the same polymer, but after exposure to 248 nm radiation in the presence of PAG (TPSNf). In the absence of PAG, poly(1-co-2) exhibits an onset temperature for decomposition of 336 °C and the copolymer exhibits considerable thermal stability even in the presence of photo-decomposed PAG. The corresponding weight loss for the protecting group (CH_3OCH_2-) is not clear from Figure 4B most probably due to its very low content (~2.6 wt%).

Lithographic performances of poly(1-co-2), with 28 mol% of monomer 2, were tested using a 248 nm stepper. Although the resist formulated with TPSNf in PGMEA exhibited poor adhesion properties on a silicon wafer, clear latent images were observed after exposure at 248 nm followed by post-exposure bake (PEB). However, it was not successful to obtain images during the subsequent development in 0.262 N tetramethylammonium hydroxide (TMAH) solution due to the poor wetting properties of relatively polar poly(1). In order to enhance adhesion as well as wettability, terpolymers were prepared using small amounts (~6 mol%) of methacrylic acid (MA). Although the presence of MA in poly(1-co-2-co-MA)

Figure 5. Structures of poly(1-co-THPMA)-based resists and feed ratios.

Figure 7. Contrast curves obtained with 1 wt% PAG.

Figure 6. SEM images obtained with poly(1₈₀-co-THPMA₂₀) (A), poly(1₇₀-co-THPMA₃₀) (B), and poly(1₆₀-co-THPMA₄₀) (C); PAG: 1 wt % TPSNf; development: 0.26 N TMAH for 60 sec.

dramatically improved both adhesion and wettability, the terpolymer was soluble in 0.262 N TMAH solution even before exposure at 248 nm. From this result, it was postulated that high dissolution selectivity can be achieved after exposure by incorporating protected methacrylic acids such as *tert*-butyl methacrylate (TBMA) or tetrahydropyranyl methacrylate (THPMA).

A series of copolymers of monomer 1 with either TBMA or THPMA were prepared by radical polymerization. As expected from the volume effect of the CF₃ group, only a modest increase in absorbances ranging from 2.03 to 2.56 μm⁻¹ was observed at 157 nm with copolymers containing 10~20 mol% of TBMA or THPMA. Preliminary screening tests using a 248 nm stepper indicated that poly(1-co-THPMA)-based resists have better lithographic performances than poly(1-co-TBMA)-based resists under similar processing conditions. Therefore, lithographic studies were focused on poly(1-co-THPMA)-based resists with different amounts of THPMA.

3.3. Lithographic Studies of Poly(1-co-THPMA)

Figure 5 shows structures and monomer compositions of poly(1-co-THPMA)-based resists.

The presence of THPMA in the copolymer is expected to reduce transparency. In order to minimize additional increase in absorbance due to the presence of PAG and THPMA, initial tests on a 248 nm stepper were carried out with poly(1₈₀-co-THPMA₂₀) which contains 20 mol% of THPMA in a feed ratio and 1 wt% TPSNf with respect to the polymer weight. In general, the addition of a base improved dissolution selectivity between exposed and unexposed regions. Therefore, trioctyl amine (TOA) was employed to control the acid diffusion in a weight ratio of TPSNf/TOA ~ 50.

After spin-coating the resist on silicon wafers, post-apply bake (PAB) was carried out at 115 °C for 90 sec. After exposure at 248 nm, PEB was carried out at three different temperatures, 90, 115, and 130 °C. When PEB was carried out at 115 °C, pattern collapse was observed with features less than 0.3 μm and this was more conspicuous with PEB temperature of 130 °C. Better results were obtained with PEB temperature of 90 °C, but top-rounding was observed as shown in Figure 6A. With poly(1₇₀-co-THPMA₃₀) and poly(1₆₀-co-THPMA₄₀), only partial resolution was observed with features below 0.5 μm as shown in Figure 6B and 6C. From the SEM images, it can be seen that

poly(**1**₇₀-co-THPMA₃₀) exhibits better resolution than poly(**1**₆₀-co-THPMA₄₀). In Figure 7, are shown contrast curves obtained using these three resists with different amounts of THPMA. It should be noted that poly(**1**₇₀-co-THPMA₃₀) and poly(**1**₆₀-co-THPMA₄₀) exhibit almost the same sensitivity or dose response. This clearly indicates that 1 wt% PAG is not enough for these two systems. This observation also corroborates to the SEM results in Figure 6 where poly(**1**₇₀-co-THPMA₃₀) displays better resolution than poly(**1**₆₀-co-THPMA₄₀). In other words, with a limited PAG concentration and therefore with less than complete deprotection, poly(**1**₇₀-co-THPMA₃₀) exhibits better resolution than poly(**1**₆₀-co-THPMA₄₀), since the ratio of acidic repeat unit/non-acidic repeat unit is higher with poly(**1**₇₀-co-THPMA₃₀).

In the next series of experiments, 3 wt% PAG was employed in the formulation with three poly(**1**-co-THPMA) copolymers and imaging experiments were carried out without changing other processing parameters. Figure 8 shows contrast curves obtained with 3 wt% PAG. With 3 wt% PAG, the clearing dose was reduced by a factor of ~3 compared to the previous system containing 1 wt% PAG. As shown in Figure 9, top-rounding was not observed with poly(**1**₈₀-co-THPMA₂₀) and more importantly even dense lines were clearly resolved down to 0.3 μm with poly(**1**₇₀-co-THPMA₃₀) and poly(**1**₆₀-co-THPMA₄₀). It is also notable that poly(**1**₆₀-co-THPMA₄₀) has better sensitivity than poly(**1**₈₀-co-THPMA₂₀) and better photo-speed than poly(**1**₇₀-co-THPMA₃₀).

3.4. Rejuvenation of 248 nm Resist Backbones for 157 nm Lithography

Lithographic studies with poly(**1**-co-THPMA) clearly demonstrate that fluorocarbon-containing acrylic backbones can be used as resist platforms for 157 nm lithography. Although etch resistance

Figure 8. Contrast curves obtained with 3 wt% PAG.

can also be imparted to the poly(**1**)-based resists by replacing the THP group with cyclic alkyl groups, this approach may have to compromise with loss in transparency due to the additional absorbance by hydrocarbons in the cyclic alkyl structure. Therefore, in an effort to find comonomers that are not only etch resistant but also transparent at 157 nm, we embarked on the study of modified styrenic monomers. Preliminary studies with silylated polystyrenes indicated that the transparency of even polystyrenic backbones can be dramatically improved by incorporation of alkyl silyl groups in the para-position. For example, the absorbance of poly(*p*-trimethylsilyl styrene) was measured to be $4.37 \mu\text{m}^{-1}$ at 157 nm and this is significantly lower than that of polystyrene ($\sim 6 \mu\text{m}^{-1}$). From this result, one can expect that, by combination of monomer **1** with modified styrenic monomers, the rejuvenation of backbones used in 248 nm resists, known arguably as the best chemically amplified resists, is possible at 157 nm lithography.

In Figure 10, is shown a VUV-VASE spectrum of poly(**1**-co-**3**), which is one of the platforms under investigation. As expected, the copolymer exhibits a strong absorbance at 193 nm due to the presence of an aromatic group. However, a sharp

Figure 9. SEM images obtained with poly(**1**₈₀-co-THPMA₂₀) (A), poly(**1**₇₀-co-THPMA₃₀) (B), and poly(**1**₆₀-co-THPMA₄₀) (C); PAG: 3 wt % TPSNf; development: 0.26 N TMAH for 60 sec.

Figure 10. VUV-VASE spectrum of poly(1-co-3).

Figure 11. SEM image obtained with poly(1-co-3); PAB 125 °C/90 sec, PEB 100 °C/60 sec, 3 wt% TPSNf, 0.1 wt% TOA, 30 mJ/cm², and 0.262 N TMAH.

drop in the absorbance is observed below 190 nm and the absorbance at 157 nm was determined to be 2.38 μm^{-1} . This clearly demonstrates that by judicious modification of strongly absorbing chromophores, such as carbonyl or aromatic, it is possible to use conventional resist backbones in the design of chemically amplified resists for 157 nm lithography. It is also interesting to note that poly(1-co-3) is ultra-transparent at 248 nm, displaying an absorbance of $\sim 0.07 \mu\text{m}^{-1}$ at this wavelength, which is significantly lower than those of commercial resists for 248 nm lithography. This can be attributed to the presence of a hexafluoroisopropyl group in monomer 3 as well as the high transmittance of a fluorocarbonol-containing acrylic backbone that exhibits an absorbance less than $0.01 \mu\text{m}^{-1}$ at 248 nm. Therefore, this type of a resist backbone can also be used for 248 nm lithography, especially in a process where thick resist films are required.

Imaging experiments were carried out with poly(1-co-3) using a 248 nm stepper. Without process optimization, isolated lines were resolved down to 0.25 μm and dense lines were clearly

Figure 12. SEM images obtained with poly(1₈₀-co-THPMA₂₀) (A) and poly(1₆₀-co-THPMA₄₀) (B).

resolved down to 0.3 μm . In Figure 11, is shown a representative SEM image obtained using conditions listed in the caption. Under these conditions, a clearing dose of this resist was observed at $\sim 30 \text{ mJ/cm}^2$. This slower photo-speed, compared to poly(1-co-THPMA)-based resists, is most probably due to the presence of ethoxy methyl ether that has higher activation energy for deprotection compared to the THP ether.

After exhaustive screening tests using a 248 nm stepper, lithographic studies using a 157 nm stepper were carried with poly(1-co-THPMA)-based resists. In Figure 12, are shown SEM images obtained with poly(1₈₀-co-THPMA₂₀) and poly(1₆₀-co-THPMA₄₀). As previously observed, top-rounding occurred with poly(1₈₀-co-THPMA₂₀), but 1:5 line and space patterns were clearly resolved down to 130 nm. With poly(1₆₀-co-THPMA₄₀), isolated lines were resolved down to 80 nm without top-rounding. These images were obtained using a binary mask and therefore it is expected that further miniaturization in feature sizes is possible with optical enhancement techniques.

4. Conclusions

It was found that fluorocarbonol-modified acrylic and styrenic monomers can be used in the design of chemically amplified photoresists, highly

transparent at 157 nm. Further improvement in transparency is possible by adding *transparency enhancers* to the resist platform, which are fluorocarbonol- or protected fluorocarbonol-containing small organic molecules. Preliminary results in 157 nm lithography proved that, with judicious molecular-level design, the synthesis of single-layer resists for 157 nm lithography is possible using simple chemistries.

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5. References

1. Kunz, R. R.; Bloomstein, T. M.; Hardy, D. E.; Goodman, R. B.; Downs, D. K.; Curtin, J. E. *J. Vac. Sci. Technol. B* **1999**, *17*, 3267.
2. Przybilla, K. J.; Röschert, H.; Pawlowski, G. *Adv. Mater.* **1992**, *4*, 239; *Proc. SPIE-Int. Soc. Opt. Eng.* **1992**, 1672, 500.
3. Ito, H.; Seehof, N.; Sato, R. *Polym. Mater. Sci. Eng.* **1997**, *77*, 449; Ito, H.; Seehof, N.; Sato, R.; Nakayama, T.; Ueda, M. *ACS Symp. Ser.* **1998**, *706*, 449.
4. Schmaljohann, D.; Bae, Y. C.; Weibel, G. L.; Hamad, A. H.; Ober, C. K. *Proc. SPIE-Int. Soc. Opt. Eng.* **2000**, 3999, 330.
5. Bae, Y. C.; Dai, J.; Weibel, G. L.; Ober, C. K. *Polym. Prepr.* **2000**, *41*(2), 1586.
6. Schmaljohann, D.; Bae, Y. C.; Dai, J.; Weibel, G. L.; Hamad, A. H.; Ober, C. K. *J. Photopolym. Sci. Technol.* **2000**, *13*, 451.
7. Snow, A. W.; Sprau, L. G.; Soulen, R. L.; Grate, J. W.; Wohltjen, H. *J. Appl. Polym. Sci.* **1991**, *43*, 1659.
8. Seebach, D. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1320.
9. Ramsey, B. G.; Taft, R. W. *J. Am. Chem. Soc.* **1966**, *88*, 3058.